

Waste Disposal Technologies for Polychlorinated Biphenyls

by Warren T. Piver* and F. Thomas Lindstrom*

Improper practices in the disposal of polychlorinated biphenyl (PCB) wastes by land burial, chemical means and incineration distribute these chemicals and related compounds such as polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) throughout the environment. The complete range of methods for disposal that have been proposed and are in use are examined and analyzed, with emphasis given to the two most commonly used methods: land burial and incineration.

The understanding of aquifer contamination caused by migration of PCBs from subsurface burial sites requires a description of the physical, chemical and biological processes governing transport in unsaturated and saturated soils. For this purpose, a model is developed and solved for different soil conditions and external driving functions. The model couples together the fundamental transport phenomena for heat, mass, and moisture flow within the soil.

To rehabilitate a contaminated aquifer, contaminated groundwaters are withdrawn through drainage wells, PCBs are extracted with solvents or activated carbon and treated by chemical, photochemical or thermal methods. The chemical and photochemical methods are reviewed, but primary emphasis is devoted to the use of incineration as the preferred method of disposal. After discussing the formation of PCDFs and PCDDs during combustion from chloroaromatic, chloroaliphatic, as well as organic and inorganic chloride precursors, performance characteristics of different thermal destructors are presented and analyzed. To understand how this information can be used, basic design equations are developed from governing heat and mass balances that can be applied to the construction of incinerators capable of more than 99.99% destruction with minimal to nondetectable levels of PCDFs and PCDDs.

Introduction

Polychlorinated biphenyls (PCBs) were developed to be chemically inert, to have exceptional dielectric characteristics, and to be resistant to degradation for long periods of time at high temperatures. For these reasons, they have been widely used as heat transfer fluids in electrical transformers, as hydraulic fluids in pumps and as heat transfer fluids in heat exchangers. They maintain their integrity over a wide range of operating conditions. After a period of use, these materials are removed for disposal.

Many approaches have been used to dispose of waste PCBs but the method of choice from the standpoint of performance is incineration. Performance data for different incinerator designs have been presented by Ackerman and Scofield (1) and Bonner et al. (2). These data indicate that destruction efficiencies for incinerators are very high when properly designed, operated, and maintained. On the other hand, Ahling (3), Ahling and Lindskog (4), Buser (5), Choudhry et al. (6) and Olie et al. (7) investigated the formation and measured concentrations of polychlorinated dibenzofurans (PCDFs) and

polychlorinated dibenzodioxins (PCDDs) in the exhaust emissions from incinerators. These same compounds, however, have been identified in PCB samples before they were incinerated (8-10), indicating that they may be found in the emissions from a poorly designed incinerator presumably because residence time, oxygen supply, turbulence, atomization, or some combination of all these factors in the reactor zone were inadequate. In this review, performance data of different incinerator designs will be analyzed to identify critical design criteria that ensure high percentages of destruction of PCBs and their contaminants and that provide conditions that do not favor formation of other toxic combustion products.

Incineration is a very expensive option. Until recently, a much less expensive option was subsurface burial. Unfortunately, this disposal method has been the source of widespread contamination of surface and groundwaters (11). Even in a well-designed subsurface burial site, protective liners and catchment systems will be breached and PCBs will gradually migrate into groundwaters. Corrective measures to purify contaminated aquifers usually include draining the aquifer, extracting the PCBs in a surface treatment plant and either chemically treating or incinerating the extract.

Figure 1 shows schematically the environmental

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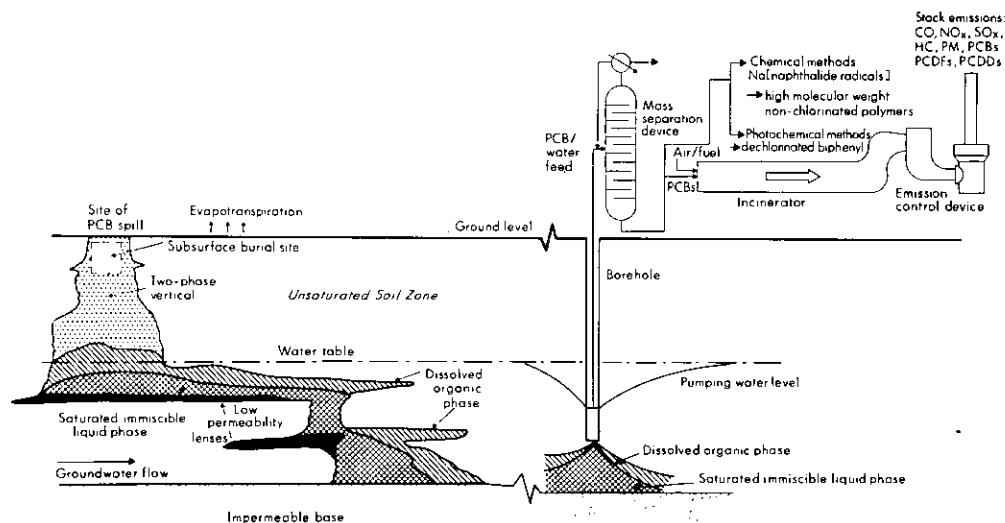


FIGURE 1. Movement of PCBs in the environment due to waste disposal activities.

impact of improper practices in subsurface burial and incineration of PCBs.

Simulating Transport of PCBs in Unsaturated and Saturated Soils

Because groundwaters are relied on heavily as sources of drinking water, contamination of these resources by toxic chemicals is a major problem in highly industrialized countries. For Japan, in 1981, 22% of the drinking water and 33% of the industrial needs were supplied from groundwater resources (12). In 1975, groundwater usage for all purposes in the United States accounted for 59% of the total water demand (13). In the future, much more attention must be given to determining the hydrogeological properties of the proposed burial site and the types of chemicals that can be buried in these sites.

Many studies have analyzed and simulated transport of solutes in unsaturated/saturated soils (14-19). In these studies, isothermal conditions were assumed, and linear relationships were introduced to treat variations in moisture content and moisture dependent properties. Because the transport phenomena are coupled, realistic simulations can only be achieved by simultaneous solution of the equations of motion describing heat, mass, and moisture transport.

In a model developed by Lindstrom and Piver (20), several important simplifications were introduced that convert the complicated nonlinear partial differential equations developed by previous investigators (14-19) into ordinary differential equations, facilitating the solution of model equations. External driving functions can be imposed at the air-soil interface—such as rainfall and periodic sunlight—making it possible to simulate the behavior of chemicals in a soil column under realistic environmental conditions. With this model, many variables that govern transport can be

changed, and it is possible to examine the behavior of solutes under a variety of conditions; for example, water solubilities for PCB mixtures at 20°C that range from 0.025 mg/L (about 25 ppb) to 0.2 mg/L (21), and linear soil adsorption rate constants for PCBs that range from 40 to 40,000 cm³ soil water/g soil, depending on the isomer present and the composition of the soil (22).

The simplifying features of the model for PCB transport in soils are: (1) the soil is partitioned into a finite number of layers of thickness, Δz ; (2) perfect mixing in each layer is assumed; (3) the bulk of the heat, mass and moisture is transferred vertically; and (4) competition between PCB isomers and other chemical for sorption sites on soil surfaces is negligible.

The visual representation of the model showing the temperature, moisture and chemical concentration fields, the partitioning of the soil column into layers and the inputs of external processes that drive solute transport in the soil column are shown in Figure 2. Moisture flow, heat flow and solute flow balances are constructed for each soil layer. The total distributions of moisture, temperature and solute concentration as functions of time and position in the soil column are determined by simultaneously solving the coupled sets of ordinary differential equations for individual soil layers.

The moisture balance equation between layer k and $k-1$ is given by Eq. (1):

$$\frac{dX_{M_k}}{dt} = A \left\{ (\bar{q}_{lz} + \bar{q}_{vz})z_{k-1} - (\bar{q}_{lz} + \bar{q}_{vz})z_k \right\} \quad (1)$$

where \bar{q}_{lz} and \bar{q}_{vz} are moisture mass flow rate vectors for the liquid and vapor state as a result of vertical gradients in moisture content, $\partial\theta/\partial z$, and temperature, $\partial T/\partial z$, dX_{M_k}/dt is the rate of change of moisture in each soil layer and A is the contact area between soil layers, the air-soil interface and the water

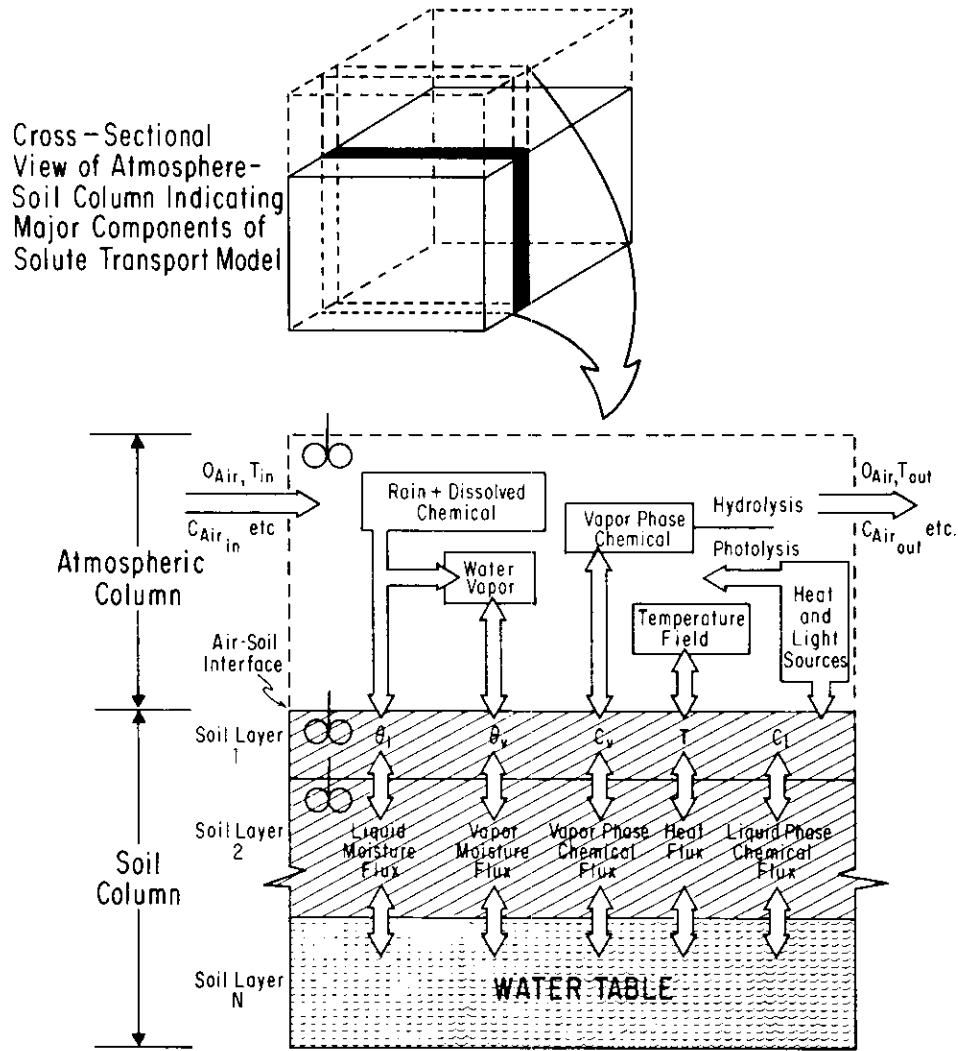


FIGURE 2. Representative element of volume used in the soil transport simulation model.

table boundary. The mass flow vectors for moisture in both the liquid and vapor states are given by Eqs. (2) and (3):

$$\vec{q}_{lz} = -\rho_w \underline{D}_{\theta_l} \frac{\partial \theta}{\partial z} - \rho_w \underline{D}_{T_l} \frac{\partial T}{\partial z} + \rho_w \underline{K}(\theta) \quad (2)$$

$$\vec{q}_{vz} = -\rho_w \underline{D}_{\theta_v} \frac{\partial \theta}{\partial z} - \rho_w \underline{D}_{T_v} \frac{\partial T}{\partial z} \quad (3)$$

where ρ_w is the density of water, \underline{D}_{θ_l} and \underline{D}_{θ_v} are second-rank tensors for the dispersion coefficients for moisture in the liquid and vapor state that are functions of moisture content and moisture tension, \underline{D}_{T_l} and \underline{D}_{T_v} are second-rank tensors for the thermal dispersion coefficients in the liquid and vapor state that are functions of moisture content and moisture tension, and $\underline{K}(\theta)$ is the conductivity tensor of the liquid that is a function of moisture content and moisture tension.

Two sets of boundary conditions are required to completely specify this problem, one at the air-soil

interface, and one at the water table interface. At the air-soil interface, moisture enters as a result of rainfall and is removed by evapo-transpiration as follows:

$$A(\vec{q}_{lz} + \vec{q}_{vz})|_{z=0} = \begin{matrix} Q_{\text{rain}}(t) \\ \text{[precipitation term]} \end{matrix} - A\theta|_{z=0} E_{\text{con}}(1 + B_{\text{vap}} WS) \rho_{wv}^{\text{Sat}}(T_a)(1 - \theta_a) \quad (4)$$

[evapo-transpiration term]

where E_{con} is vaporization of water constant, B_{vap} is the rate of vaporization, WS is wind speed over the surface, T_a is the air temperature and θ_a is the moisture content of the air.

At the water table, the mass flow rate vector for water is given by Darcy's law as:

$$\vec{q}_{lz}|_{z=WT} = \rho_w \underline{K}(\theta)|_{z=WT} \quad (5)$$

The corresponding heat balance for each soil layer accounts for the transfer of heat in both the liquid and vapor phase. The two modes of heat transfer that describe energy transfer are conduction and convection and the heat balance between layer k and $k-1$ is given as:

$$\frac{dX_{H_k}}{dt} = A \left\{ C_H + (\mathcal{L} + c_{\text{vap}}T)\vec{q}_{vz} + c_{\text{liq}}\vec{q}_{lz}T \right\}_{z_{k-1}} - A \left\{ C_H + (\mathcal{L} + c_{\text{vap}}T)\vec{q}_{vz} + c_{\text{liq}}\vec{q}_{lz}T \right\}_{z_k} \quad (6)$$

where C_H is the conduction of heat in the soil and water phases and given as:

$$C_H = -(1 - \epsilon)\lambda_{\text{soil}}(\partial T/\partial z) - \lambda_w\theta(\partial T/\partial z) \quad (7)$$

In most instances, conduction of heat in the vapor phase is negligible. Other terms in this expression are \mathcal{L} for latent heat of vaporization, c_{vap} and c_{liq} are the heat capacities for water vapor and water, respectively, λ_{soil} and λ_w are heat conductivities for soil and water, and dX_{H_k}/dt is the rate of change of heat content in each soil layer.

At the air-soil interface, the boundary condition is:

$$A(C_H + (\mathcal{L} + c_{\text{vap}}T)\vec{q}_{vz} + c_{\text{liq}}\vec{q}_{lz}T|_{z=0}) = Q_{\text{rain}}(t)c_{\text{liq}}\rho_w T_{\text{(RW)}} + A(1 - \alpha)q_{\text{SWR}} - Q_{\text{htesl}} - Q_{\text{htlws}} - Q_{\text{htssl}} + Q_{\text{htlwra}} \quad (8)$$

where:

$$Q_{\text{rain}}(t)c_{\text{liq}}\rho_w T_{\text{(RW)}} = \text{heat transfer due to rainfall} \quad (9)$$

$$A(1 - \alpha)q_{\text{SWR}} = \text{net radiative heat transfer to the soil surface} \quad (10)$$

$$Q_{\text{htesl}} = A\mathcal{L}\theta_0(0.001\rho_w/\rho_{\text{air}})[1 - B_{\text{vap}}(\text{WS})]\rho_{\text{wv}}^{\text{Sat}}(T) \times \left[1 - \frac{\theta_a\rho_{\text{wv}}^{\text{Sat}}(T_a)}{\rho_{\text{wv}}^{\text{Sat}}(T_{\text{soil}})} \right] = \text{evaporative heat loss from soil surface;} \quad (11)$$

$$Q_{\text{htlws}} = A\epsilon_{\text{soil}}\sigma T^4 = \text{longwave radiation heat loss from the soil surface} \quad (12)$$

$$Q_{\text{htssl}} = A\rho_{\text{air}}c_{\text{air}}D_h(T - T_a) = \text{sensible heat loss} \quad (13)$$

$$Q_{\text{htlwra}} = A\epsilon_{\text{air}}\sigma T_a^4 = \text{longwave radiation heat loss in the air above the soil} \quad (14)$$

where θ_0 is the initial moisture content, σ is the Stephan-Boltzman content, ϵ_{soil} and ϵ_{air} are the emissivities of the soil and air, D_h is absolute humidity and c_{air} is the heat capacity of the air.

The boundary condition at the water table for the rate of heat transfer is:

$$H_{sz} = c_{\text{liq}}\rho_w \left(\frac{K(\theta|_{z=WT})T|_{z=WT}}{T} \right) \quad (15)$$

In a similar manner, the mass balance for each soil layer describing transport of solubilized chemical is given as:

$$\frac{dX_{C_k}}{dt} = \quad (16)$$

$$A(\vec{J}_{C_l} + \vec{J}_{C_v})|_{z_{k-1}} - A(\vec{J}_{C_l} + \vec{J}_{C_v})|_{z_k} - C_l\Lambda$$

where \vec{J}_{C_l} and \vec{J}_{C_v} describe transport as a result of dispersion and convection and Λ is a term describing removal of the solubilized chemical as a result of biodegradation, irreversible sorption, chemical reaction and/or hydrolysis.

The mass flux vectors are defined as:

$$\vec{J}_{C_l} = -\underline{D}_{C_l}(\partial C_l/\partial z) + \vec{V}_{lz}C_l \quad (17)$$

$$\vec{J}_{C_v} = -\underline{D}_{C_v}H_c(\partial C_l/\partial z) + \vec{V}_{vz}H_cC_l \quad (18)$$

where \underline{D}_{C_l} and \underline{D}_{C_v} are second-rank tensors for the dispersion coefficients for liquid and vapor, \vec{V}_{lz} and \vec{V}_{vz} are liquid and vapor velocity vectors and from Henry's Law, $C_v = H_cC_l$, has been used to specify vapor phase concentration, where H_c is the Henry's Law constant.

The removal term, Λ incorporates biotic and abiotic processes and is defined as:

$$\Lambda = V_k[(\rho_B/\epsilon)(\beta_l\theta + \beta_v(\epsilon - \theta)H_c)] + V_k[(\rho_B/\epsilon)(\gamma_l\theta + \gamma_v(\epsilon - \theta)H_c)] + V_k[\alpha_l\rho_w\theta + \alpha_v(\epsilon - \theta)H_c\rho_{\text{wv}}^{\text{Sat}}] \quad (19)$$

Here, the first term on the right-hand side is for biodegradation, the second is for adsorption and chemical reaction and the third is for hydrolysis. V_k is the volume of soil in the k -th layer, ρ_B is the bulk density of the soil, β_l and β_v are liquid and vapor phase biodegradation rate constants, γ_l and γ_v are liquid and vapor phase adsorption/chemical reaction rate constants, α_l and α_v are liquid and vapor phase hydrolysis rate constants, and h is the relative humidity.

At the air-soil interface, the boundary condition is given as:

$$A(\vec{J}_{C_l} + \vec{J}_{C_v})|_{z=0} = Q_{\text{chem in}}(t) + A\Omega \quad (20)$$

where $Q_{\text{chem in}}$ is the amount of chemical added to the top layer of soil as a function of time and Ω is the amount sorbed to the soil interface. Ω is defined as:

$$\Omega = \theta K_{\text{vap}}(H_cC_l - C_a) + (\epsilon - \theta)\eta(H_cC_l - C_a) = (H_cC_l - C_a)[\theta K_{\text{vap}} + (\epsilon - \theta)\eta] \quad (21)$$

where K_{vap} is the vaporization rate constant at the soil

Table 1. Run control variables that were held constant during simulation runs.

Symbol	Meaning	Value-dimensions
H_c	Henry's law constant	1.73×10^{-7} (dimensionless)
D_{l0}	Liquid phase molecular diffusion coefficient	$0.084 \text{ cm}^2/\text{hr}$
D_{v0}	Vapor phase molecular diffusion coefficient	$252.4 \text{ cm}^2/\text{hr}$
K_{vap}	Vaporization rate constant as soil-air interface	$1 \times 10^5 \text{ } \mu\text{g}/\text{hr}$
V_a	Volume of air chamber	$6.375 \times 10^3 \text{ cc}$
A	Area of contact between soil layers	7500 cm^2
C_a	Volumetric air flow rate	$2.4 \times 10^7 \text{ cm}^3/\text{hr}$
WS	Wind speed	$1.412 \times 10^3 \text{ cm}/\text{hr}$
β_{vap}	Vaporization of water due to wind	$1.0 \text{ hr}/\text{cm}$
E_{con}	Vaporization of water constant	$1.26 \text{ cm}/\text{hr}$
β_{vap}	Temperature effect of saturated vapor	$1.05 \times 10^{-6} \text{ g}/\text{cm}^3\text{-}^\circ\text{K}$
α_{Albedo}	Albedo of soil surface	0.05 (dimensionless)
ϵ	Soil porosity	0.44 (dimensionless)
ρ_b	Bulk density of soil	$1.35 \text{ g}/\text{cm}^3$
ϵ_{soil}	Emissivity of soil	0.98 (dimensionless)
θ_{sat}	Saturated moisture content	0.44 (dimensionless)
$K(\theta_{\text{sat}})$	Saturated water conductivity	$0.33 \text{ cm}/\text{hr}$
ϵ_{water}	Emissivity of water	0.95 (dimensionless)
% sand	Percent of sand in soil	0.682 (dimensionless)
% clay	Percent of clay in soil	0.193 (dimensionless)
% org	Percent of organic matter in soil	0.125 (dimensionless)

interface, ϵ is soil porosity and η is the vapor phase mass flow rate at the soil-air interface.

At the water table, the steady-state boundary condition is:

$$\partial(\bar{J}_C)/\partial X = C_L A \quad (22)$$

At the water table, transport is in a horizontal direction and this equation can be solved very simply to give (14,23):

$$\frac{C_i(L)}{C_{i0}} = \exp \left\{ \left(\frac{L}{2a_L} \right) \left[1 - \sqrt{1 + 4\lambda a_L (\epsilon/q)} \right] \right\} \quad (23)$$

where a_L (q/ϵ) has been substituted for D_{C_i} , a_L is dispersivity, $q/\epsilon = \bar{V}_{Lz}$, and $C_i(L)$ is concentration at a location, $z = L$, downstream from the entry point.

Using the Simulation Model to Predict PCB Movement in Soils

The model intitled TCMOD (20) allows great flexibility regarding selection of soil characteristics and external rainfall and light events that drive transport in the unsaturated soil zone. With this model, the rain schedule included seven rain events that occurred over a period of 60 days at a frequency of one every eight days. Rainfall occurred over a 10-hr interval and produced 1 in. of rain/event (at this rate, average annual rainfall would amount to 45 in. of rain, a rate typical of a temperate climate). For the 60 days of this simulation, the daylight-darkness schedules were the same; 14 hr of daylight followed by 10 hr of darkness.

For the simulation runs, a Geary silt loam soil was chosen because data were available from de Wit and van

Table 2. Run variables.

Run no. ^a	Dispersion coefficient, cm	Adsorption coefficient, cm ³ soil/cm ³ water
1	0.1	400.0
2	0.1	4000.0
3	1.0	400.0
4	1.0	4000.0

^aFor each run, the daylight-darkness schedule and the intensity of solar radiative heat input were constant. For each set of dispersion and adsorption coefficients the temperate climate rain schedule (1 in/event) was used.

Keulen (24) for moisture tension and water conductivity as functions of moisture content and soil depth. The moisture tension function and the water conductivity functions were approximated as:

$$\psi(\theta, z) = \alpha_\theta(z) \left\{ 1 - [\theta_{\text{sat}}(z)/\theta(z)]^{\beta_\theta(z)} \right\} \quad (24)$$

and

$$K(\theta, z) = K(\theta_{\text{sat}}, z) \left\{ [\theta(z)/\theta_{\text{sat}}(z)]^{\gamma_{\text{con}}(z)} \right\} \quad (25)$$

where $\psi(\theta, z)$ is the moisture tension function, $\alpha_\theta(z)$ is a constant with a value of 30.0 cm; $\theta_{\text{sat}}(z)$ is the moisture content of the soil at saturation with a value of 0.44 weight percent; $\theta(z)$ is the moisture content at depth z ; $\beta_\theta(z)$ is a power law constant determined from a regression analysis of the data from de Wit and van Keulen (24) with a value of 6.0; $K(\theta, z)$ is the water conductivity function that approximates the second-rank tensor representation for $K(\theta)$ introduced in Eq. (2); $K(\theta_{\text{sat}}, z)$ is the water conductivity at saturation with a value of 0.33 cm/hr; and $\gamma_{\text{con}}(z)$ is a power law constant with a value of 11.5 determined by a regression analysis of the data from de Wit and van Keulen (24).

Table 1 lists the variables that were held constant throughout the simulation along with the values that

were used and their dimensions. Table 2 lists the variables that were changed from run to run. They include the dispersivity coefficient, and the adsorptivity coefficient that is a function of soil composition.

The most difficult components of this model to simulate were the processes that remove chemicals as a result of biotic and abiotic transformation. In many cases, specific data were not available or had to be deduced from data that were gathered under conditions that made extension to field conditions difficult. For example, there have been several studies on *in vitro* bacterial degradation of PCBs and related compounds (25-27) in the presence of nutrients and carbon sources that support microbial growth. In the top 1 to 2 cm of soil, nutrients and usable carbon sources are most plentiful. Depending on the degree of chlorination and available carbon sources, within the time frame of the study, biotic reactions range from partial dechlorination for monochlorobiphenyls, dichloro isomers, and some trichloro isomers to no alteration for the highly chlorinated isomers (25). Because PCBs are difficult carbon sources for soil microbes to use, biotic degradation of these chemicals is probably a secondary process. Isomers with four or more chlorines, however, do not appear to be altered even by secondary processes.

If these chemicals lie on the surface of the soil, photochemical degradation must be considered as a

potential removal process. Photochemical decompositions have been studied with the use of ultraviolet light sources, but they do not proceed at appreciable rates unless an effective hydrogen source is available (29-32). In the top layer of soil, hydrogen sources are available in most soils, and degradation of the more chemically reactive PCBs (e.g., 1,3-chloro isomers) occurs to an extent that is a function of the degree of chlorination and the position of the chlorine atoms relative to the linkage between the two benzene moieties of the molecule. The highly chlorinated isomers most likely are unaltered by either biotic or photochemically induced degradation in the top layer of soil.

At the present time there are insufficient data to determine if degradation of PCBs occur at soil depths beneath the top soil layers. In the subsoil layers, sufficient biomass is available (33), even though it has been suggested that the populations of bacteria decrease with depth (34). Bacteria in the subsoil layer, however, are at survival levels and probably do not have the appropriate metabolizing enzymes, although they may be inducible. Because of the lack of specific data on biotic and abiotic removal of highly chlorinated biphenyls, mechanisms for degradation by all processes were approximated by first order processes, with the rate constant for microbial degradation chosen as $1.0 \times 10^{-6}/\text{hr}$; that for chemical reaction, as $1.0 \times 10^{-7}/\text{hr}$.

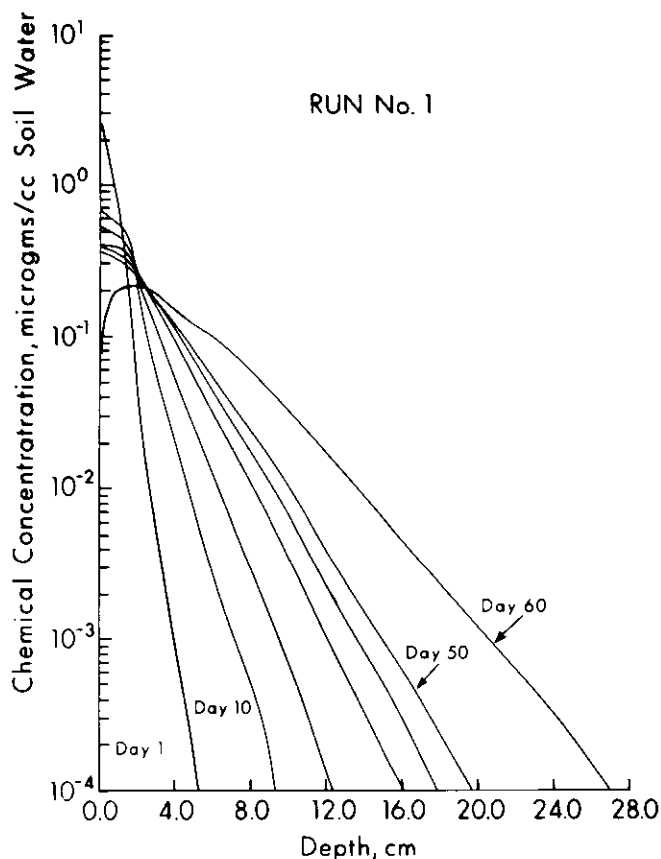


FIGURE 3. PCB transport in soils with low dispersion and adsorptivity coefficients

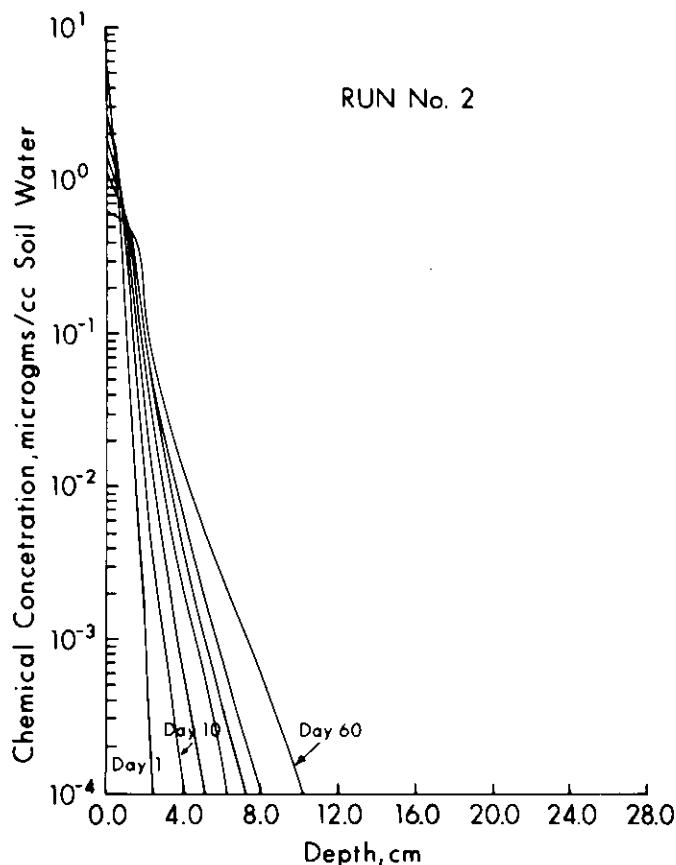


FIGURE 4. PCB transport in soils with low dispersion and adsorptivity coefficients

Another major question in using this model is the water solubilities of PCBs isomers. If solubilities or quantities of material are greater than 10^{-3} mole/L, equations would need to be included for each solute because interactions between aqueous and organic phases become important. For small concentrations, use can be made of the correlation between solubility and partition coefficient (35). PCBs have partition coefficients that range from 4.6 to 6.7, yielding a solubility range in water of 8×10^{-5} to 8×10^{-7} mole/L. At these solubilities, PCBs are present at concentrations that make it possible to use a single solute model to predict behavior for the entire group of PCB chemicals. Because of this simplification, this model should not be applied to predict migration in soils from massive surface spills such as the one reported by Roberts et al. (36).

Figures 3-6 present examples illustrating transport of small amounts of PCBs in soils with different dispersion and adsorption characteristics, a situation similar to the slow migration from a subsurface burial site. In each run, a rain schedule of 1 in. of rain every 8 days and a constant sunlight/darkness schedule were used. Downward migration through the unsaturated soil is typical of that expected for a soil that is alternately moistened and dried by these events. During infiltration of moisture the PCBs are driven down

into the soil and continue to move downward until the drying process causes a reversal in mass flux that never completely returns the concentration profile to its original state. Over a very long time, depending on the hydrologic and adsorptive capacities of the soil and frequency and intensity of rain, these chemicals reach the groundwater flow. Because of differences in hydrology and adsorptivity of unsaturated soils, however, the time of arrival at the water table is shorter for a low adsorptivity high dispersivity soil than for a high adsorptivity low dispersivity soil for the same frequency and intensity of rainfall. Because PCBs have very low rates of degradation, essentially all the material that enters the groundwater flow will be recovered at locations far downstream if the time interval is long enough. This same type of behavior has been observed with the unsaturated aliphatic solvents, trichloroethylene and tetrachloroethylene (33,37).

For a large-scale surface spill of PCBs, the top layers of the soil will be exposed to high concentrations of the chemical dissolved in an organic solvent. Terms must be included in the transport equations to account for transport of a large water insoluble phase and a vapor phase composed of volatized PCBs and organic solvent. The model that has been developed in this report is not equipped to represent large surface spills. For a large spill, PCBs will be present in a dissolved aqueous

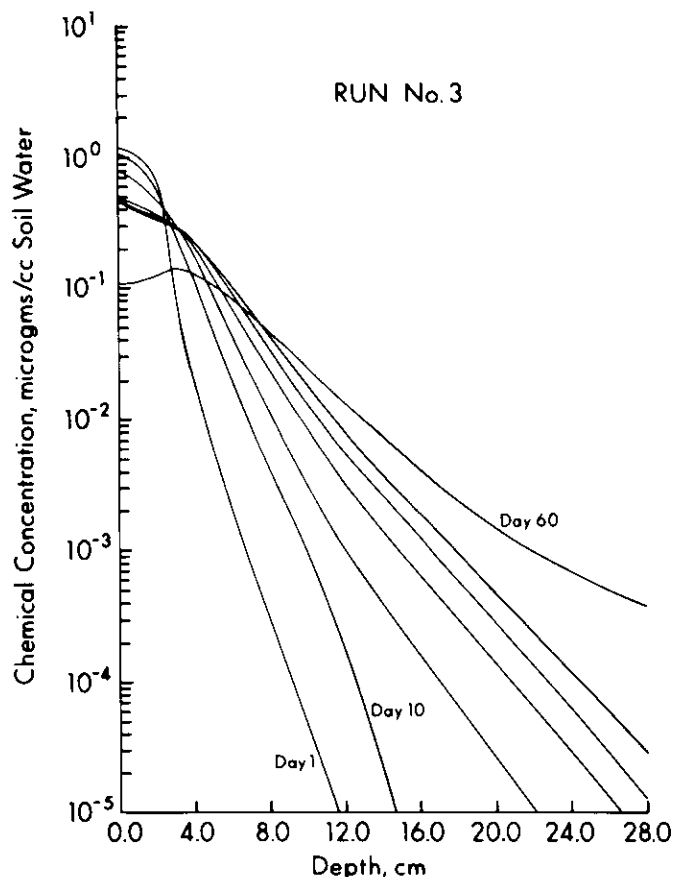


FIGURE 5. PCB transport in soils with moderate dispersion and low adsorptivity coefficients

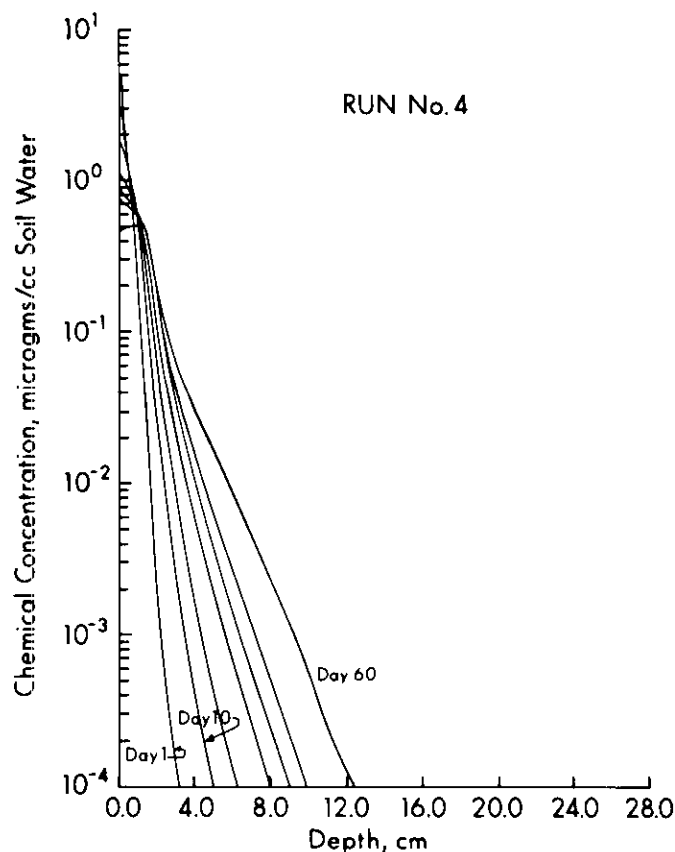


FIGURE 6. PCB transport in soils with moderate dispersion and high adsorptivity coefficients

phase, an adsorbed phase, and a water insoluble solvent phase (36). In the model presented in this investigation, the rate of entry of PCBs from a subsurface burial site is very slow, making it possible to neglect multiple phase and multiple component transport and to treat PCBs in waste as very dilute solutions. Small amounts also make it possible to neglect competitive effects for adsorption sites on soil surfaces. For a spill, however, the interactions between soil constituents and the solvent cannot be neglected, and competitive effects for adsorption sites on soil surfaces are important.

Carefully designed soil column and field studies of PCB transport to validate this transport model are limited. Tucker et al. (38) used laboratory soil columns to study PCB migration in three different soils. The results indicated that after a 4-month interval, the effluents from a saturated sandy loam and silty loam soil were in the range of the water solubilities for Aroclor 1016, a PCB product containing less of the highly chlorinated isomers. From this study, for a silty clay loam soil, PCBs were not detected after 4 months, indicating a high degree of adsorption may have occurred. Data on soil transport properties were not available. Column experiments must be designed to represent many different possible field conditions. Low water conductivity, high adsorptivity layers such as clay soils should be underlain by high water conductivity, low adsorptivity soil layers, a condition not uncommon in field situations. When clay layers become saturated, significant concentration gradients are established and much of the stored chemicals will be transmitted to an underlying high water conductivity low adsorptivity soil layer. However, because the packing of laboratory columns can significantly influence the hydrodynamics, they should not be overinterpreted.

Purification of Contaminated Aquifers

Because of the dispersed nature of groundwater systems, purification of a contaminated aquifer will be a very costly and time-consuming process. Unlike surface waters that have well-defined boundaries, groundwater systems have boundaries that are governed by submerged hydrogeological factors not easily detected from surface features. The complexities of an unconfined aquifer are illustrated in Figure 1. Not only is it necessary to account for multiple phase flow in the unsaturated zone of the soil, but in the saturated zone of the soil high permeability lenses can exist that rapidly conduct groundwater, nonaqueous phases, and dissolved materials.

To establish a network of drainage and counter gradient wells to remove contaminants requires a very extensive examination of the hydrogeology of the area. Included in this examination are studies to determine the adsorption-desorption characteristics of soils in different zones of the soil because these characteristics will profoundly effect the ease and time required to flush contaminants from the aquifer. A detailed knowl-

edge of adsorptive capacities of different regions of the soil cannot be over-emphasized. Adsorption-desorption studies with 2,4,5,2',4',5'-hexachlorobiphenyl reported by DiToro and Horzempa (39) indicate that a definite fraction of this class of chemicals can be very tightly bound to many types of soil in a manner approaching irreversible binding. Because of this, the desorption process will require a very long time and can result in a gradual release of these compounds into an aquifer over protracted intervals.

The purification of a contaminated aquifer includes two operations (40). In the first, wells are drilled to determine the hydrogeology of the region and to establish a monitoring network. Once the extent of contamination is determined, the aquifer is pumped dry through properly positioned drainage wells. If a drinking water supply is threatened by a contaminant plume, the perimeter of the zone is determined and injection wells are placed along the boundary. Several drainage wells are placed within this boundary to draw off contaminated water. Injection wells facilitate drainage and can be arranged and used to establish counter gradients preventing further aquifer contamination. Before the contaminated water can be discharged or used, PCBs and other contaminants must be extracted. The separation, concentration, and/or chemical or thermal degradation of PCBs constitute the second set of operations involved in purification. Because PCBs will be present in low concentrations, a large amount of water must be processed.

Surface Technology for Rehabilitation and Disposal of PCB Wastes

Liquid extraction with isopropanol has been used to remove PCBs from contaminated groundwater, but for most purposes, extraction by adsorption on packed or fixed beds is more effective. For very low aqueous concentrations, other separation technologies should be evaluated. Reverse osmosis is a possibility, but all separation technologies must be evaluated because data are not available for removal efficiencies at low initial concentrations. If incineration is used to dispose of PCB wastes, then facilities will be required to handle PCBs adsorbed to carbon particles, not an impossible problem but one requiring a somewhat different approach from the situation in which PCBs are introduced in liquid form. In either case, the design and operation of the appropriate separation equipment for multicomponent systems are available from McCabe and Smith (41) and Belfort et al. (42).

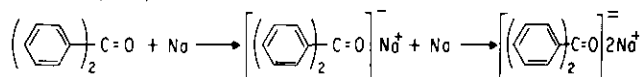
Chemical and Microbially Mediated Methods of PCB Decomposition

Brooks (43) has recently reviewed the chemical and biological methods of PCB destruction. The majority of the chemical methods depend on the preparation of a

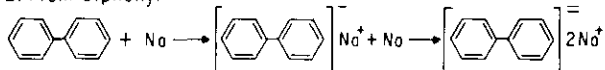
DECHLORINATION OF PCBs BY ORGANOSODIUM REAGENTS

I Formation of Sodium Organic Reagents

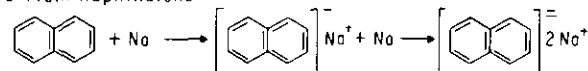
A. From diphenyl Ketone



B. From biphenyl



C. From naphthalene



II Dechlorination of PCBs with Sodium Naphthalene

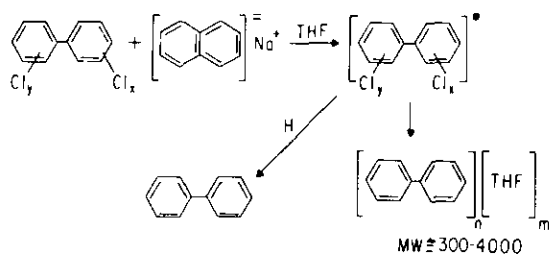


FIGURE 7. Chemical methods of PCB dechlorination with organosodium reagents.

sodium reagent to remove chlorine atoms from the PCB molecule and are designed for more concentrated mixtures of PCB isomers than would be encountered in contaminated groundwaters. Of these methods, the most feasible one uses anion radicals to dechlorinate the PCB molecule. The technique developed by Oku et al. (44) involves the initial preparation of sodium naphthalide in an ethereal solvent such as tetrahydrofuran (THF) which protects the very reactive sodium naphthalide from contact with oxygen and water. For this technique to be effective with PCBs extracted from groundwater, they must be concentrated and be free of moisture to avoid the violent reaction between sodium and water. Brooks (43) has suggested that excessive drying of PCBs can be eliminated by mixing the PCBs, naphthalene and an oil dispersion of sodium in a single step at room temperature. By using a well-stirred, water-jacketed reactor, high temperatures produced by this exothermic reaction can be effectively controlled. The process chemistries for different variations of the method are given in Figure 7. Reaction products are NaCl and a high molecular weight polymer of unknown structure and chlorine content.

Another method that has been used to decompose PCBs (43) is the repeated nucleophilic displacement of a chlorine by a thiolate anion or hydroxyl group. The products of the reaction are reported to be polyhydroxybiphenyls (43). Both of these chemical methods are expensive and may be feasible for small quantities of concentrated PCB wastes. For very large problems such as the decontamination of an aquifer, other methods are more feasible.

Photochemical processes for destruction of PCBs, PCDDs, and PCDFs are initiated by an ultraviolet light source that causes a homolytic cleavage of the carbon-chlorine bond. For decomposition to proceed, however, a hydrogen source must be available. In the presence of either methanol or hexane, which are effective hydrogen donors, decomposition of the above compounds proceeds at a very rapid rate (29-32). The products of the reaction are the chlorinated hydrogen donors, e.g., a polychlorinated methanol, or polychlorinated hexane, along with stripped PCB, PCDD, and PCDF molecules. Limitations on concentrations of PCB waste that could be effectively treated and performance data for each method were not presented.

To eliminate the problem of formation of chlorinated solvents, Kitchens et al. (45) patented a process that uses hydrogen gas and short-wavelength ultraviolet radiation. Because the biphenyl reaction product inhibits the reaction, it is removed continuously by distillation. The process is effective for waters that are contaminated with PCBs to a maximum level of 3500 ppm. Completeness of destruction is monitored by performing a determination of PCB content in the reaction mixture with GC-MS. The kinetics of the reaction are not rapid and very large reactor vessels are required to provide sufficient retention times for decomposition.

Methods that use soil bacteria have demonstrated marginal ability to degrade PCBs, especially the highly chlorinated derivatives. With cultured bacteria, Yagi and Sudo (46) have observed that mono- and dichlorobiphenyls (Aroclor 1221 and 1232) have a half-life of 8 days, with 90% destruction achieved within 15 days. With tri- and tetrachlorobiphenyls (Aroclor 1242, 1248, and components of 1254) reductions of 50% are achieved in 30 days, with 90% destruction requiring greater than 60 days. For penta- and higher substituted biphenyls (Aroclor 1260 and components of 1254), reductions of 50% require time periods that are greater than one year. As a surface treatment technology for contaminated aquifers, degradation rates are too slow for these methods to be considered feasible. Concentration limits in which microbial techniques would be effective were not discussed, but the rate of decomposition is very likely a function of the total biomass that is available and the characteristics of the microbial population.

Thermal Destruction of PCB Wastes

By far the greatest attention in recent years on methods of disposal of PCBs and other toxic wastes has been given to the use of incineration. It has been demonstrated, however, that incineration of chloroaromatic precursors such as PCBs and chlorobenzenes can or may produce polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (4-6). Evidence also exists for the formation of these compounds from nonchlorinated aliphatic precursors and inorganic chlorine during incineration or thermo-

chemical processing of these materials (6). The data relating to the formation of PCDDs and PCDFs during incineration suggest that formation is the result of pyrolysis. In an oxidizing environment with combustion air in excess of stoichiometric requirements, and elevated temperatures destruction of PCBs to HCl and CO₂ is a possible—and indeed favorable—reaction thermodynamically (1). The problem for design of incinerators is to provide the appropriate set of design and operating conditions that ensure oxidizing conditions, ensure maximum atomization and turbulent mixing of reactants, and ensure sufficient temperatures and retention times that permit the oxidation reaction to proceed to a high level of completion.

Thermal Destructors

In Table 3, incinerators of different designs are listed. Included in this table are data on combustion chamber temperature, retention times, destruction efficiencies for PCBs, and the levels of PCDFs and PCDDs that have been detected in exhaust emissions. At the present time, only limited attempts have been made to analyze the design and operating features of incinerators that promote high levels of PCB destruction and minimize formation of more toxic combustion products. The final EPA rules for PCB incinerators (47) now govern performance, but do not consider hardware design except as it pertains to automatic cutoff valves for feeding chemicals into the incinerator when monitored exhaust emissions begin to exceed specified emission standards.

Conventional thermal technologies are divided into two categories. In the first category, the only function of the incinerator is the thermal destruction of the waste chemical. In the second category, the technology provides more than one function. With this distinction, cement kilns are placed in the second category because the thermal destruction of PCBs produces HCl that is used to neutralize the basicity of cement.

A third category is the novel or developmental processes (48). Technologies in this class include devices that do not have commercial scale experience but are based in most instances on well-established principles. Fluidized bed incinerators, molten salt reactors, and plasma reactors are several examples of technologies in this class. The molten salt reactor produces inorganic compounds which are very easy to dispose of, whereas the plasma reactor operates at very high reactor zone temperatures (5000°C) that completely destroy a compound in the plasma zone of the reactor. Very special attention to the conditions in the relaxation zone downstream from the reactor zone of this device are required, however, to prevent formation of products that can be more toxic than the starting materials. Fluidized beds offer more even and uniform mixing of reactants making it possible to use lower combustion zone temperatures to achieve high destruction efficiencies and longer residence times, but require performance data on formation of PCDDs and PCDFs.

Formation of PCDDs and PCDFs during Combustion of PCBs

In an oxidizing environment, the formation of PCDDs and PCDFs from PCBs, and other chloroaromatic precursors and aliphatic compounds plus inorganic chlorides, is not a favorable process thermodynamically (1). This is not to say that it is impossible, because thermodynamics does not require kinetic models to determine if processes happen or not. The probability of formation at elevated temperatures in an oxidizing environment with greater than stoichiometric amounts of air present, however, is extremely low. Even so, there are data that refute this position and which raise several important issues that must be carefully considered in the design of incinerators or other thermal devices used to decompose PCB wastes (5-7,49-55). On the other hand thermochemical calculations confirm that forma-

Table 3. Characteristics of thermal destructors for PCBs.

Type	Combustion chamber temperature, °C	Retention time, sec	Destruction efficiency for PCBs, %	Comments on performance	Reference
Commercially available methods					
Chemical waste incinerator	1100-1200	2 sec	99.99-99.999	Best system for liquid waste injection; PCDFs for PCDDs not detected	(1)
Shipboard incineration	1500-1600	1-2	99.999	PCDFs or PCDDs not detected; can handle 6000 kg/hr of liquid, 3000 kg/hr solids	(56)
High efficiency boilers	1430-1675	1-3.7	99-99.99	PCDFs or PCDDs not detected; detection limits 10 ⁻⁴ mg/m ³ ; feed limits: 50-500 ppm	(61)
Cement kilns	2100	30	99.99986	Best system; HCl neutralizes basicity of cement; PCDFs or PCDDs not detected; feed limits determined by acid needs of cement	(1, 3, 55)
Experimental designs					
Molten salt	840-982		99.9999	PCDFs or PCDDs not detected; best results when ash content low	(47)
Fluidized bed	590-600		99.9999	Potential only for liquid PCBs; limestone reacts with combustion gases	(47)

tion of PCDDs and PCDFs are favored when pyrolytic conditions exist in these devices (1).

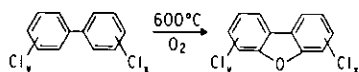
The mechanisms for formation of PCDDs and PCDFs from PCBs and other precursors have been studied by Choudhry et al. (6). In Figure 8 these proposed chemical reaction mechanisms are presented. From these studies, the formation of PCDFs from PCBs is a relatively simple process of intramolecular cyclization with oxygen at temperatures of 600°C with yields of 1 to 3%. The mechanism of PCDD formation from PCBs involves a more complex mechanism, the first step being decomposition of PCBs to chlorinated benzene radicals. The bimolecular mechanism proposed by Buser

(5) provides a possible explanation for the formation of PCDDs and PCDFs from these radicals at elevated temperatures.

Performance data assembled in Table 3 include both the level of destruction of PCBs and the presence and concentration of PCBs, PCDFs, and PCDDs in exhaust emissions. Freeman (48) has recently presented performance data for selected innovative thermal destructors listed in this table. Additional performance data for cement kilns have been taken from reports by Ahling (3), Ahling and Lindskog (4) and McDonald et al. (56). Johnson et al. (57) reported on the performance of shipboard incineration, and Ackerman and Scofield (1) reported on the performance of a wide range of thermal destructors for PCBs and many other chloroaromatics. More recent performance testing with land and shipboard incinerators, however, has found PCDFs and PCDDs in exhaust emissions because more exacting analytical procedures were used.

FORMATION OF POLYCHLORINATED DIBENZO FURANS (PCDFs) AND POLYCHLORINATED DIBENZO DIOXINS (PCDDs) FROM PCBs AND OTHER CHLOROAROMATIC PRECURSORS

A. Formation of PCDFs from PCBs



B. Formation of PCDFs and PCDDs from PCBs and Chlorinated Benzenes

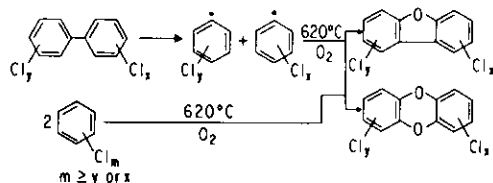


FIGURE 8. Possible mechanisms of formation of PCDFs and PCDDs during high temperature incineration of PCBs and chloroaromatics.

Design Criteria for PCB Incinerators

From a phenomenological standpoint, incineration is an extremely complex process involving simultaneous heat and mass transfer with many competing and series chemical reactions. Incineration of PCBs includes pyrolysis and oxidation. The main problems in design are to provide proper contacting patterns, sufficient reaction time, and sufficient uniform temperatures to minimize pyrolysis and minimize oxidation.

The proper design of an incinerator includes two

INCINERATOR DESIGN FEATURES

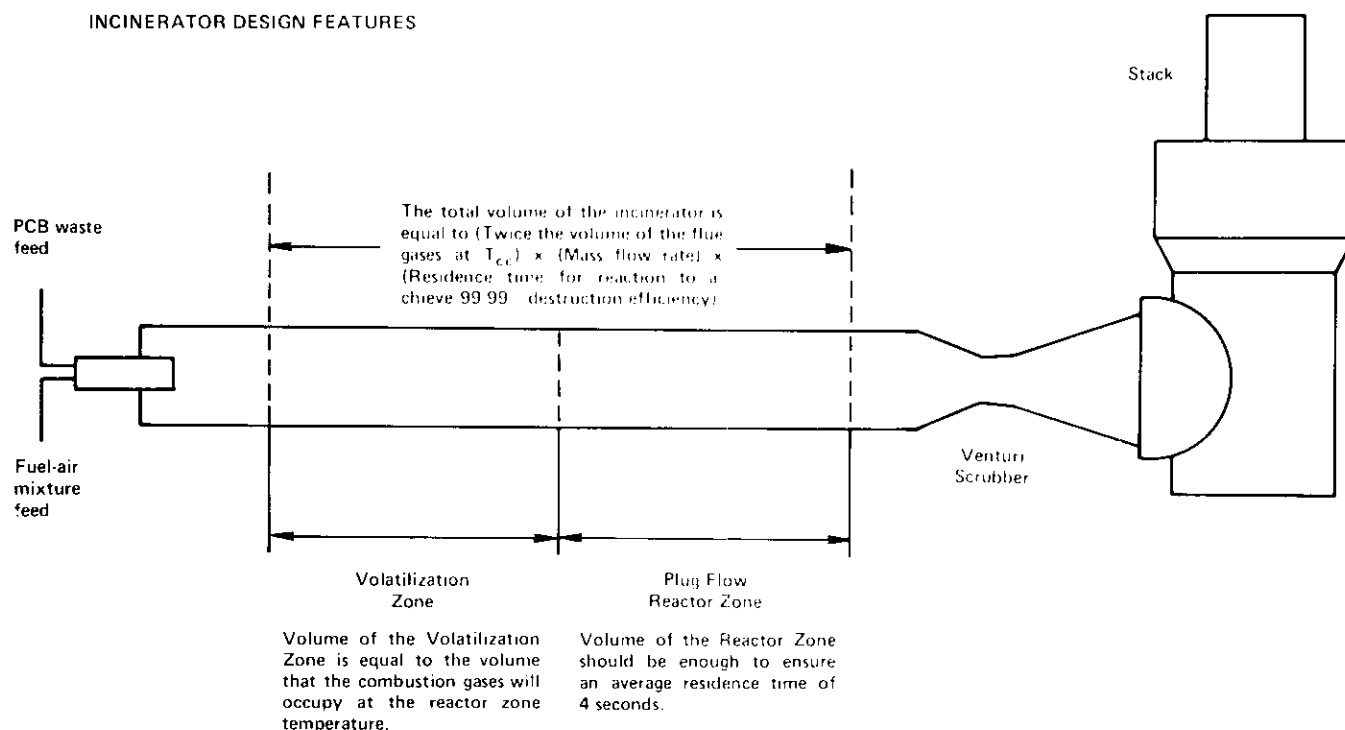


FIGURE 9. Basic design features of PCB incinerators.

zones, a volatilization zone and a reactor zone. The main function of the volatilization zone is to preheat the waste stream and ensure that it is in a highly dispersed state. There must be enough space for the expansion of liquid vapors from ambient temperatures to the combustion chamber temperatures and for the generation of highly dispersed micro-sized particles from solid materials. Temperature control in this region of the incinerator is important but not as critical as in the reactor zone. To achieve the proper residence time, degree of turbulence, and reaction temperature the reactor zone should be designed to be as close as possible to an idealized isothermal plug flow reactor. This reactor configuration ensures maximum conversion because maximum turbulence and uniformity of temperature are achieved throughout the entire length of the reactor zone. The contacting patterns of this reactor are very closely approximated by the land-based and shipboard incinerators presented in Table 3. Diagrammatically, the important features and functions of high performance incinerators are represented in Figure 9.

Work of Duvall et al. (58) indicates that temperatures in excess of 600°C are required before significant thermal decomposition of 2,4,5,2',4',5'-hexachlorobiphenyl occurs in air and that temperatures in excess of 800°C are required to achieve destruction levels of 99.99% as specified in the EPA regulations for incinerator performance (47). Temperatures in excess of 800°C are also necessary to achieve high levels of destruction of hexachlorobenzene, a PCDD precursor. These kinetic data, however, were generated with non-flame conditions and in a laboratory reactor that had a very high surface area to volume ratio. Because of the possible catalytic effects contributed by the reactor surface, temperatures in excess of 1000°C and residence times of greater than 3 sec are recommended in design calculations.

The procedure for design of incinerators can either follow the method outlined by Danielson (59) and Bonner et al. (2) or use design equations for isothermal plug flow reactors presented by Levenspiel (60). Because Levenspiel's method requires a very detailed knowledge of reaction kinetics for the thermal decomposition of PCBs, the procedures outlined by Danielson (59) and Bonner et al. (2) will be used.

For accurate determination of the combustion air requirements, the heating value of the PCB waste stream must be known or calculated. Low molecular weight PCBs have a very high heating value, but as the chlorine and moisture content increase the heating value decreases very rapidly. An excessive amount of moisture can reduce the combustion chamber temperature below that required for decomposition. For these reasons, provisions are made for PCB solid and liquid wastes to be co-fired with heating oil and high heat content solvents. The heating value in units of kcal/kg and the effects of chlorine and moisture content can be determined empirically from the Dulong Formula (61) as follows:

Heating Value (HV), kcal/kg =

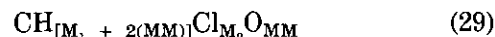
$$14095.8 \times (\text{weight fraction of carbon}) + 54677.6 \times (\text{weight fractions of hydrogen}) - \frac{1}{8} \times (\text{weight fraction of oxygen}) + 3981.6 \times (\text{weight fraction of sulfur}) + 2136.6 \times (\text{weight fraction of oxygen}) + 1040.4 \times (\text{weight fraction of nitrogen}) - 454.8 \times (\text{weight fraction of chlorine}) \quad (26)$$

If the molar formula for the PCBs to be incinerated is given as: $\text{CH}_{M_1}\text{Cl}_{M_2}$, where M_1 and M_2 are the moles of hydrogen and chlorine, respectively, relative to one mole of carbon, the total molecular weight of the waste stream, including moisture is:

$$\text{Molecular weight} = \frac{[12 + M_1(1) + M_2(36.5)]}{[1 - \text{weight \% moisture (WPM)}]} \quad (27)$$

$$\text{MM} = (\text{TMW} - \text{MW of PCBs})/18 \quad (28)$$

where TMW is the molecular weight of the waste stream, e.g. PCBs plus moisture, WPM is weight percent of moisture and MM is the number of moles of moisture in the waste stream. Then the moles of oxygen and moles of hydrogen are MM and 2MM, respectively, and the final molar formula is given as:



The stoichiometric air requirement for complete combustion in terms of mass of air/mass of waste are given as:

$$\text{SA} = \frac{137 \left\{ 1 + \frac{[M_1 + 2\text{MM}]}{4} - \frac{\text{MM}}{2} \right\}}{12 + 2M_1 + 2\text{MM} + 36.5M_2 + 16\text{MM}} \quad (30)$$

The theoretical air requirements (TA) in units of mass of air/mass of waste are given as:

$$\text{TA} = 1 + \text{SA} \quad (31)$$

because the amount of ambient air must be taken into account in a balanced equation for the combustion process. From the molar formula for the waste system the heating value can be calculated.

With this information, the calculation of the feedrate to achieve a desired combustion temperature of 1000°C involves a solution of the coupled steady-state heat and mass balances for this process. Using the steady-state mass balance, the total mass flow rate of PCBs (W_{PCBs}), is given as:

$$W_{\text{PCBs}} = F_o \left[\left(1 - \frac{\text{WPM}}{100} \right) \left\{ 1 + \left(1 + \frac{\text{EA}}{100} \right) \text{SA} \right\} + \frac{\text{WPM}}{100} \right] \quad (32)$$

where F_o is the PCB waste stream feedrate; WPM is weight percent moisture in the feed; EA is percentage

of excess air in the combustion air stream and SA is the stoichiometric air requirement in units of mass of air/mass of waste.

From the steady-state heat balance equation, the net heat transferred in units of kcal/hr or Btu/hr is given as:

$$Q_{\text{Net}} = F_o \left[HV \left(1 - \frac{\text{WPM}}{100} \right) (\text{HL}) - \text{LHV} \left\{ \frac{\text{WPM}}{100} + \left(1 - \frac{\text{WPM}}{100} \right) \left(\frac{M_1 + 2(\text{MM})}{4} \right) \right\} \right] \quad (33)$$

where HV is the heating value of the waste, LHV is the latent heat of vaporization, and HL is the percent heat loss through the walls of the incinerator by conduction, convection, and radiation. HL is estimated as:

$$\text{HL} \approx 1.25(1/\ln F_o) \quad (34)$$

This expression holds well for flow rates between 80 and 120 lb/hr, but for flow rates greater than 120 lb/hr, heat loss by conduction, convection, and radiation is approximately equal to 20% of the gross heat input. Using these approximations and substitutions, the steady-state heat transfer rate and the combustion chamber temperature are:

$$W_{\text{PCBs}} c_p (T_{\text{CC}} - T_{\text{amb}}) = Q_{\text{Net}} \quad (35)$$

and by arrangement:

$$T_{\text{CC}} = \frac{Q_{\text{Net}}}{W_{\text{PCBs}} c_p} + T_{\text{amb}} \quad (36)$$

where c_p is heat capacity of the combustion gases at the combustion chamber temperature and T_{Amb} is the ambient temperature. In these two equations, the feed rate F_o of PCBs cancels out, and combustion chamber temperature is only a function of the heating value of the waste stream (including moisture) and the amount of excess combustion air. The greater the amount of excess air and moisture in the waste stream, the lower the combustion chamber temperature.

The volume of the incinerator can be determined by calculating the volume of the flue gases at the combustion chamber temperature using the ideal gas law and Charles' law. At 20°C, the flue gases generated by the combustion process will occupy the volume/unit mass given by the ideal gas law as:

$$V_{\text{FG}}|_{T=20^\circ\text{C}} = \frac{\left[1 + \left(1 + \frac{\text{EA}}{100} \right) \text{SA} \right]}{\text{TMW}} \left(\frac{RT_{20}}{p} \right) \quad (37)$$

where TMW is total molecular weight of the waste; R is the gas constant; T_{20} is absolute temperature at 20°C = 293°A; and P is pressure.

The volume of flue gases/unit mass at the combustion chamber temperature is given by Charles' law as:

$$V_{\text{FG}}|_{T=T_{\text{cc}}} = \left(V_{\text{FG}}|_{T=20^\circ\text{C}} \right) \left(\frac{T_{\text{cc}} + 273}{T_{20}} \right) \quad (38)$$

The total volume of the incinerator is given as:

$$V_{\text{In}} = 2V_{\text{FG}}|_{T=T_{\text{cc}}} \cdot F_o \tau \quad (39)$$

where τ is the residence time in hours. A factor of two is required because the total volume of the incinerator includes the volume required for expansion of the flue gases plus an equal volume for combustion reactions.

Because many assumptions were made to calculate this volume, standard practice adds an overdesign factor to achieve a longer average residence time than is determined experimentally. Longer residence times and high levels of turbulence are necessary to achieve better destruction efficiencies because the kinetics of destruction and formation of toxic by-products are not well understood. Using higher combustion temperatures creates problems of excessive NO_x formation, and the introduction of too much excess air can produce temperatures that are too low for maximum destruction. There are, however, opportunities to fine tune the operating conditions of feedrate and excess air to correct any observed deficiencies. In addition, auxiliary fuel can be added to maintain proper temperature in the combustion zone. Because of this capability, the only requirement on the stack emissions is the use of a wet scrubber for HCl. The details of design of these devices employ steady-state heat and mass balances and procedures are outlined in Danielson (59).

Conclusions

In this review, different methods of waste disposal for PCBs and their limitations have been examined. Of these methods, incineration offers the most potential because destruction efficiencies can be very high and the amount of residue left for disposal after combustion is completed is negligible for well-designed and operated unit. Clearly the worst option is subsurface burial because of nondegradability and long-lasting contamination of groundwaters with PCBs.

The disadvantages of incineration are cost and formation and emission of combustion products such as polychlorinated dibenzofurans (PCDDs) and polychlorinated dibenzodioxins (PCDDs), that are much more toxic than their chloroaromatic precursors. Even though the design process is not as precise as desired and must rely on steady-state heat and mass balances for coupled transient phenomena, when units are improperly designed and operated, formation and atmospheric release of these chemicals are almost a certainty. Even in well-designed and well-operated units, however, these chemicals may be formed but at much lower levels. Incinerators with uniformly distributed temperatures due to a high degree of turbulent mixing, and adequate residence times for reactions to proceed to a high level of destruction are the best possible option for disposal. Achieving these design and operating conditions requires careful attention to detail, a basic understanding

of the factors that control destruction efficiencies and influence contaminant formation, and a well-designed program for training operators and monitoring incinerator performance.

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